FLUORINE MODIFICATION OF ZEOLITE CATALYSTS

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ABSTRACT

The introduction of fluorine into the zeolite phase can significantly change the catalytic activity of the zeolite. The dependence of the catalytic activity of modified samples on the fluorine content was determined for acidic-type reactions. In addition, the acidic centers in the fluorinated zeolites were studied using microcalorimetric measurements of the heat of ammonia adsorption. For ZSM 5-type zeolites the influence of an assumed ordered center distribution on the activity is discussed.

INTRODUCTION

Fluorine is often used as a component and a modifier of catalysts [1]. During the last few years some fluorine modifications of zeolites have been described.

Araya et al. [2] studied zeolites containing occluded salt molecules, introduced to the inner zeolite structure by means of heating in molten salts. They found that unlike samples containing Cl^- and NO_3^-, only some of the occluded F could be removed by water elution from the zeolite phase. The authors suggested that two different fluoride species had been incorporated into the lattice.

Sariev and coworkers [3-5] reported on their modifications of zeolite catalysts with diluted HF aqueous solutions. Normally the catalytic activity of the samples was increased after a mild fluorination. However, introduction of larger amounts of fluorine caused a decrease in catalytic activity and usually in crystallinity. The authors considered the possibility of bonding fluorine to the framework Al atoms or to the cations present in the zeolite.

Lok et al. [6, 7] used diluted gaseous fluorine at nearly room temperature for zeolite fluorination. They found that the properties of the fluorine-modified zeolites can be controlled by the fluorination

conditions and the post-treatment conditions. Under severe treatment conditions zeolites usually showed high dealumination, hydrophobicity of the surface, reduction in catalytic activity and changes in crystalline structure. Under mild conditions catalytic activity for n-butane cracking was significantly enhanced.

We also found in our earlier investigations a significant influence of fluorine presence on the catalytic activity of zeolites [8-12]. The samples of AlY zeolites fluorinated using NH_4F solution without prior calcination showed a considerable increase in catalytic activity for cumene cracking. A sample preheated before fluorination showed low activity and poor crystallinity. We believe that fluorine reacts mainly with Al-bearing cations yielding the catalytically active products still present in the inner zeolite structure [8, 9].

According to our experiments [10] fluorination of HY zeolite usually brought about a reduction of both crystallinity and catalytic activity. HY zeolites modified with Al cations before fluorination, however, showed a good crystallinity and high activity for cumene cracking [11].

Fluorination of H-mordenite by means of NH_4F aqueous solution or by treatment with gaseous CHF_3 resulted in a significant increase of activity for cumene cracking. The maximum increase of activity was observed for the sample containing about 0.4 wt. % of fluorine. A further increase of the fluorine content caused a decline of activity. Calorimetric measurements of the heat of ammonia adsorption showed a generation of new stronger acidic centers. We believe that during the fluorination some of the acidic OH groups were substituted with fluorine. The number of the hydroxyl groups was reduced, but the strength of the remaining ones was enhanced due to the inductive effect of fluorine [12].

The aim of the following study is to determine the influence of fluorination on the catalytic properties of ZSM 5-type zeolites. The samples were prepared by BASF according to its patent [13].

The patent authors have found that polyamines as templating agents can produce ZSM-type zeolites of well-ordered Al atom distribution. Such a structure can be obtained if the SiO_2/Al_2O_3 ratio has a specified value dependent on the templating amine used. In these so-called "isotactic" forms the distances between the Al atoms should be similar to those of the NH_2 groups in the amine molecules. We have some evidence that this well-ordered Al distribution stimulates a "geometric" selectivity in catalytic reactions of appropriate molecules. Therefore, it seemed interesting to check the influence of fluorination on this kind of selectivity.

EXPERIMENTAL

Samples of ZSM-5 zeolites, supplied by BASF and labeled as ZBM 10/4 and ZBM 12/1, were taken as starting materials. 1,6-diaminohexane and 1,3-diaminopropane, respectively, were used as templates during the preparation. The respective silica to alumina rations of the initial samples were 32.2 and 25.3. These values correspond to those of an isotactic structure.

The samples were calcined at 500° C to remove the remainders of the template. Samples labeled ZBM 10/4F1, -F2, -F3, and ZBM 12/1F1, -F2, -F3, were modified with fluorine by means of NH_4F aqueous solutions. In the case of sample 10/4FG gaseous CHF_3 was used for fluorination [10, 12, 13]. The conditions of the fluorination procedure and the properties of the samples under study are summarized in Table 1.

Table 1

Sample	Conditions of Modification	F-Content Weight %	SiO_2/Al_2O_3 Ratio
10/4		0	32.2
10/4F1	8g zeolite, 160ml 0.025M NH_4F-solution for 20h at room temperature, 12h at 100°C, 12h at 450°C in air stream	0.18	34.5
10/4F2	8g zeolite, 5x160ml 0.1M NH_4F-solution for 5x12h at room temperature, 12h at 100°C, 12h 450°C in air stream	0.23	36.4
10/4F3	8g zeolite, 160ml 0.1M NH_4F-solution for 20h at room temperature, 12h at 100°C, 12h at 450°C in air stream	0.25	36.5
10/4FG	8g zeolite, calcined in He-stream at 450°C, treated with 500ml CHF_3 (diluted with He) at 260°C for 6h	0.30	
12/1		0	25.3
12/1F1	as for 10/4F1	0.18	35.7
12/1F2	as for 10/4F2	0.53	33.8
12/1F3	as for 10/4F3	0.47	36.7

The crystallinity of the samples was examined by X-ray diffraction The calorimetric measurements of the heat of ammonia adsorption for selected samples were carried out with a Calvet microcalorimeter using a volumetric method for the estimation of the amount of adsorbed ammonia. Results are shown in Figure 1.

The catalytic properties of the modified samples were examined for hexadiene isomerization and cumene cracking. Both test reactions were

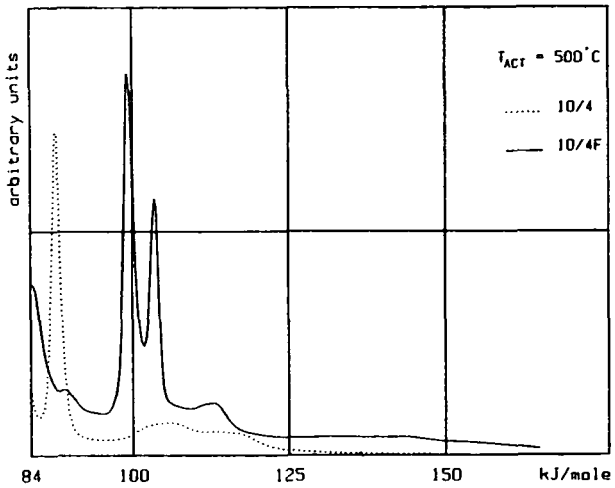

Fig. 1. Section of acidity spectra of ZBM 10/4 and ZBM 10/4F1 (concerning the strongest sites)

carried out using pulse microreactors. 20 mg of the catalyst (particles of 0.125-0.25 mm in diameter) were activated in a helium stream (300 ml/min) for 7 h at 450°C before the reaction. 1 µl pulses of hexadiene isomers (1,3; 1,5 and c1,4) were injected at the reaction temperature of 150°C. For the cumene cracking, 10 mg of powder samples were heated at 450°C for 1 h prior to reaction in a helium stream (80 ml/min). Reaction tests were carried out at 350°C. 10 pulses of 1 µl were injected and in addition pulses at 200° and 250°C were applied. The results are presented in the Figures 2 and 3.

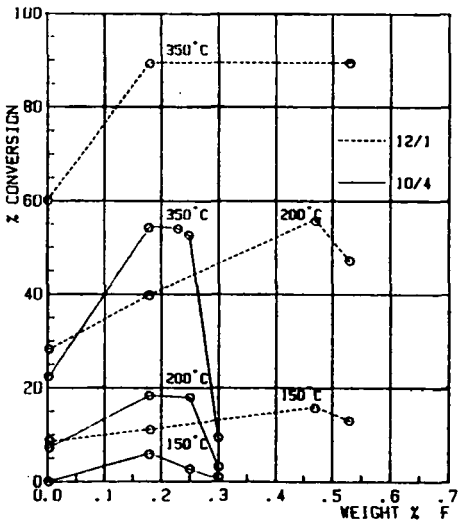

Fig. 2. Correlation between cumene cracking and fluorine content of catalyst

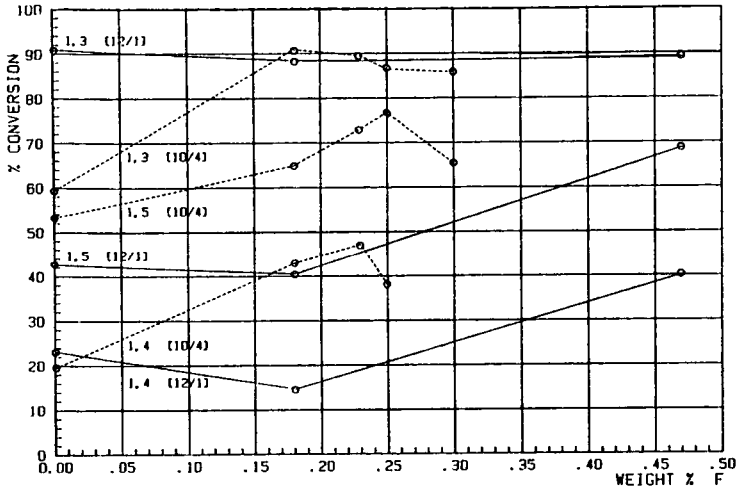

Fig. 3. Correlation between isomerization of hexadienes and fluorine content of catalyst

RESULTS AND DISCUSSION

According to the X-ray diffraction data the fluorine introduced to the ZSM-type zeolite does not affect significantly the crystalline structure. The intensities of the diffraction peaks for the fluorinated samples are similar to those of the initial ones.

The procedure applied for fluorination of ZBM zeolites was very similar to that of H-mordenite [12]. The amounts of fluorine introduced, however, are much smaller. The maximum of fluorine content for the 12/1 zeolite was about 0.5 %, whereas in the case of 10/4 it was only 0.25 % (using NH_4F solution for fluorination). The Si/Al ratio of 10/4 is higher than that of 12/1, but in the case of 12/1 this ratio increases during the fluorination process probably due to dealumination. The comparison of the maximum amounts of fluorine for both ZBM zeolites and H-mordenite leads us to the conclusion that a correlation exists between the Si/Al ration (which corresponds to the number of OH groups in the applied H-forms) and the capability for fluorine incorporation. The higher the framework Al content, the larger the amount of fluorine that can be introduced to the zeolite.

Such a correlation supports our supposition concerning fluorine-modified H-mordenite and suggests that the fluorine is introduced to the zeolite mostly by the substitution of OH groups. In the case of ZSM-type zeolites a similar method of fluorine incorporation is very likely. However, dealumination observed for the 12/1 series probably involves different sites of the zeolites framework for fluorination.

It may be worthwhile to mention that for fluorination with CHF_3

even a temperature as low as 260° C is sufficient to introduce fluorine, although Mc Vicker [14] suggested that the cleavage of a C-F bond is only possible at temperatures higher than 400°C.

The increase of activity is very pronounced in the case of cumene cracking, where strong Brønsted acid sites are involved. The activity of unfluorinated ZBM 12/1 is more than twice as high as that of ZBM 10/4. This difference can result from the higher content of acidic OH-groups in the first sample. Introduction of only 0.18 wt % of fluorine results for both zeolites in a strong increase of cumene conversion, observed even at low temperatures. The further incorporation of fluorine does not considerably change the activity of modfied samples. In the case of ZBM 10/4, however, a very sharp decrease of cumene conversion is seen above 0.25 Wt % of fluorine content whereas the sample 12/1 is still active above 0.5 % of fluorine. Some decrease in activity can be seen only at lower reaction temperatures. In our latest experiments, however, we prepared additionally a fluorine modified sample, containing more than 1 % of fluorine (a sample of ZBM 12/1F3 was fluorinated again with NH_4F). The decrease of activity for cumene cracking was very drastic, similar to the case of the 10/4 series (6 % conversion at 300°C, traces at 200°C, and 0 % at 150°C). Very similar catalytic behavior was observed in our investigation of fluorine-modified H-mordenite [12].

It is interesting to compare the catalytic activity of ZBM 10/4 and ZBM 12/1 for the reaction of 1,3-, 1,4- and 1,5-hexadiene and cumene with regard to the postulated differing distribution of the acidic centers in these zeolites. The comparison relates to the unfluorined forms and samples with the same fluorine content.

According to the concept of Marosi [13], under "isotactic" synthesis conditions such structures will be formed in which a favored arrangement of AlO_4^- tetrahedra is stimulated by the $NH_3^+ \ldots NH_3^+$ distances of the applied diamines. The corresponding acidic centers within the channel structure should show similar distances.

Concerning the isotactic 10/4 and 12/1 zeolites, the distances between the active centers of ZBM 10/4 are comparable to the distance of double bonds in 1,5-hexadiene, whereas for 12/1 a better fitting exists with 1,3-hexadiene. The distance between the double bonds in 1,4-hexadiene is similar to neither the center-to-center distances in the 10/4 nor in the 12/1 structure.

From Figure 4, in which the hydrocarbon conversion for one and the same reaction on both types of catalysts is compared, it is evident that for the non-fluorinated samples the ZBM 12/1 prefers the 1,3-con-

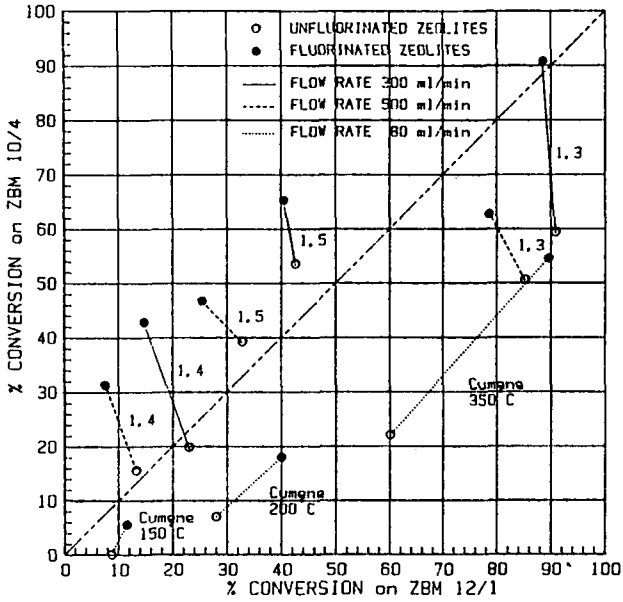

Fig. 4. Comparison of activity of fluorinated and unfluorinated ZSM 5-type catalysts for hydrocarbon reactions

version, whereas the ZBM 10/4 favors 1,5-conversion. Isomerization of 1,4-hexadiene proceeds for both catalysts with about the same yield. Since cracking of cumene involves only one acidic center a higher conversion is achieved with ZBM 12/1 because this type has a higher concentration of acidic centers due to its smaller SiO_2/Al_2O_3 ratio. In the case of cumene cracking the distances between centers are inconsequential.

The 10/4 and 12/1 types behave differently upon fluorination. Whereas ZBM 10/4 shows the expected increase in activity induced by fluorine, a slight decrease in activity occurs with 12/1. Chemical analysis of 12/1 and 12/1F1 (see Table 1), however, shows that in this case the fluorination is associated with dealumination. This probably causes an additional disturbance in the sequence of centers which could explain the observed reduction in the catalytic activity for 12/1. Since cumene cracking is independent of the ordering of the centers, the influence of the increase in acidity due to the fluorine presence dominates so that here an increase in activity results for both ZBM 10/4F1 and ZBM 12/1F1.

The increase in the catalytic activity of the fluorinated zeolites is more pronounced for cumene cracking than for hexadiene isomerization. The acidity spectrum presented in Figure 1 shows a generation of new, much stronger acidic centers after the fluorination. These newly

created centers are involved in catalyzing the cumene cracking, which requires strong acidic sites, and for this reason the fluorination effect on the catalytic activity for the cumene reaction is markedly stronger than that for isomerization.

The explanation of the nature of fluorine-bearing species introduced to the inner zeolite structure needs more extended investigation, including NMR-measurements.

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